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MECHANICAL STRENGTH OF SILICA XEROGELS

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Abstract

Mechanical strengths have been measured for silica xerogels using 4-point bending. The silica xerogels studied are microporous with open porosity of 53 vol %. Strengths were measured on fresh samples, samples which had been outgassed at 250°C, samples which were exposed to ambient conditions for 2 days, and samples stored in ethanol. Fresh samples had strengths about 20 MPa which increased to 32 MPa with outgassing but returned to 20 MPa after exposure. The loss of strength could be arrested but not reversed by storing the samples in ethanol.

Introduction

For some time now, there have been claims that monolithic silica xerogels are suitable as hosts for organic dye molecules (1,2) and as preforms for large scale optics (3). In order to realize such applications, there must be reproducibility and reliability for large populations of samples. In order to address the questions of reproducibility and reliability an evaluation of mechanical strengths and strength distributions was undertaken.

Previously studies have reported strengths of silica gels prepared from aerogels (4,5), colloidal gels (6) and xerogels (7,8). Aerogel refers to those gels prepared by hydrolyzing alkoxides and extracting the solvents during hypercritical evacuation. Xerogel refers to gels resulting from hydrolysis of alkoxides, polymerization, shrinkage and drying by slow evaporation. Primarily, these studies have followed the increase of strength as the porosity is removed during densification.

The strength of aerogels derived from solutions of tetramethyl orthosilicate (TMOS) increased from 10^{-3} MPa when dried to 100 MPa when dense (5). The strength of colloidal gels prepared from colloidal silica and potassium soluble silicate increased from 2 MPa to 100 MPa when dense (6). The strength of gels prepared from solutions of tetraethyl orthosilicate (TEOS) increased from 10^{-1} MPa when wet (9) to 20 MPa when dry (10). Silica xerogels of 50 vol % porosity prepared from solutions of TEOS after thorough drying typically have strengths of 20 MPa (7,8). All materials exhibit a strength of about 100 MPa when substantially densified.

The strength of porous materials is usually related to the load bearing cross section, but other factors such as particle coordination number, particle radius, neck radius and pore shape have to be considered. An example of how difficult it is to predict mechanical behavior in gels is a study which compares modulus of rupture for colloidal gels vs polymerized TEOS gels during aging (11,12). The modulus of rupture (MOR) in the colloidal gels was 0.01 MPa after 2 weeks of aging while the MOR in the polymerized gels was 0.14 MPa after a few days. The polymerized gel showed elastic behavior which was attributed to chemical bonding, rather than hydrogen bonding in colloidal gels which showed permanent deformation. In neither case is the microstructure of the dried gel likely to match the geometries assumed in simple models of a composite made up

of solid plus pores. However, finding a suitable physical model is not the focus of this study.

Even when a better physical model exists, there is further complication of the mechanical behavior of xerogels from the fact that the interior surface is more or less covered with silanols. The silanols which result from rehydrating siloxane bonds lead to a weakening of the gel. At the same time, the silanols may be crowded into narrow pores and actually stiffen the gel (10). It is important to note any dimensional changes which occur in gels since what appear to be inert, stable gels may expand and contract seemingly at will.

Recognizing that the mechanical behavior of gels is complicated by the nature of the porosity and the sensitivity to moisture, it was decided to prepare gels all in the same way, all having the same volume porosity (13). Large populations of samples were tested to follow their behavior as a function of time exposed to ambient humidity. Changes in dimension and weight were noted. Large populations, typically 50 samples, were broken to obtain representative strengths and strength distributions. Weibull statistics were applied to have some information about flaw populations (14).

Experimental Techniques

The preparation of silica xerogels has been described previously (13). Xerogels were prepared from nitric acid catalyzed solutions of TEOS. The molar ratio of water to TEOS was 16. Some xerogels were outgassed at 250°C for 24 hours.

Physical properties of the samples have also been described previously (13,15). Immediately after outgassing xerogels had a bulk density of 1.06 g/cm³, open porosity of 53 vol %, and a specific surface area of 900 m²/g. Porosity was almost completely microporous (less than 2.0 nm in diameter) and

cylindrical in shape. The diameter at the center of the outgassed rod shaped xerogels was 5.6 mm and the length was about 33 mm. The rods were tapered slightly from top to bottom. Linear shrinkage of the gel due to outgassing was 2.2%.

Xerogels with three different amounts of moisture were fractured. To prepare the driest samples, xerogels were infiltrated with dehydrated ethanol immediately after outgassing. During the infiltration time of about 24 hours the xerogels were in sealed vials to prevent adsorption of atmospheric moisture. These infiltrated xerogels were occasionally wetted with ethanol during fracture to prevent drying. Fresh xerogels were prepared by sealing the xerogels in tubes immediately after outgassing. These xerogels had a weight increase of about 0.5% after fracture. Xerogels of greatest moisture content were prepared by exposing them to ambient moisture for about 2 days, at which time no further weight gain was recorded. Outgassed xerogels as well as xerogels which were not outgassed were exposed to relative humidity (RH) of about 50% and a weight gain of 26% was recorded. Outgassed xerogels of 25% weight gain were stored in ethanol to see if the effect of exposure could be reversed.

Strengths were measured in a four-point flexure fixture. The fixture had a support span of 2.540 cm (1.000") and a load span of 1.270 cm (0.500"). The fixture had one degree of motional freedom to allow symmetrical distribution of stress in the specimens. Samples were fractured on a gear driven table top universal materials tester*. Silica xerogels were all fractured at a crosshead speed of 0.0508 cm/min (0.02"/min) which corresponds to a strain rate of about 3×10^{-4} /sec. Strengths were calculated from the usual expression for strengths of rods in 4 point bending

* Instron Model TTCL M4, Canton, MA.

$$S = 8P (L - a)/3.1416 D^3$$

(1)

where S is stress, P is load, L is support span, a is load span and D is the sample diameter. Fifty samples were fractured except in the case of the samples continually wetted with ethanol. Only twenty samples were fractured wet.

Vickers hardness was measured on the dry samples*. Test parameters were an impact speed of 0.3 mm/sec, an indent time of 30 sec, and a load of 1.0 kg. All samples were left in rod shape and were rested on a V-block. The values as determined by the instrument software were corrected for cylindrical surfaces. Values were reduced by as much as 3% after correction. The number of samples per test was 10 and each sample was indented once.

Results

Xerogels exposed to ambient humidity gained weight by adsorbing water. Both fresh gels and outgassed gels showed the same tendency. Figure 1 shows the weight gain for a typical sample. No further weight gain was measured after about 2 days for a given relative humidity. Samples were exposed to a variety of relative humidities. In each case, it took about 2 days to reach a constant weight. The total weight gain vs relative humidity is shown in Figure 2. Ordinarily, samples were stored in glass vials with screw caps so that the exposure to ambient humidity could be controlled.

Along with weight gain, the dimensional changes on exposure were noted. Outgassing caused linear shrinkage of 2.2%. Exposure to 35% RH caused 0.3% linear contraction and exposure to 55% RH after exposure to 35% RH gave a cumulative linear contraction of 2.0%. When the exposed sample was soaked in ethanol it expanded 0.6%.

* Zwick Hardness Tester, Model 321 2.00, Old Saybrook, CT 06475.

The Table lists the strength distributions of porous silica xerogels fractured at a strain rate of 3×10^{-4} /sec, as represented by the two parameter Weibull analysis. For each set, the mean strength, the Weibull modulus (m), and the correlation coefficient of the Weibull fit (R^2) is given. Figure 3 gives a comparison of the fresh xerogels with and without outgassing. The outgassed exposed gel has the lower Weibull modulus. Both of the sets that were exposed to ambient moisture exhibited strengths of about 20 MPa. Outgassing resulted in some widening of the distribution, as evidenced by the reduced Weibull modulus. Figure 4 shows outgassed gels with and without exposure to ambient humidity. The xerogels that were kept sealed after outgassing and gained less than 0.5% mass during a brief exposure while being measured had a mean strength of 32 MPa. The xerogels that were stored in ethanol immediately after outgassing had a mean strength of 48 MPa. Xerogels that were stored in ethanol after exposure had strengths of about 20 MPa.

The Table also lists the Vickers hardness measurement. The exposed xerogels had lower hardness than the unexposed xerogels. Outgassing did not make a difference in the hardness of exposed gels.

Discussion

The flexure strength of porous xerogels as measured at a strain rate of 3×10^{-4} /sec is very sensitive to exposure to atmospheric moisture. Even an increase in mass as small as 0.5% decreased the strength of the porous xerogels. The difference between the distributions of outgassed, exposed xerogels and fresh, exposed xerogels is attributed to surface damage and densification caused by outgassing. The strengths are about the same but the outgassed samples have a lower Weibull modulus.

The tendency for water to enhance crack growth in silica is well known.

At slow crack velocities, water corrodes siloxane bonds at the crack tip as it adsorbs in the form of silanols. It is the partial pressure of water along with the applied stress intensity that determine the rate of this reaction (16). Additionally, water is known to adsorb on the surface of silica as silanol even without application of stress (17,18).

The flexure strength of 20 MPa observed for exposed xerogels is similar to that reported in other studies. However, the strength of close to 50 MPa observed for porous xerogels stored in dehydrated ethanol is remarkably high. Ethanol molecules do not contribute to crack growth. It is found that a molecule has the ability to enhance crack growth if it is small enough to reach the crack tip and can also donate both electrons and protons. Molecules which meet these criteria include water, methanol, ammonia, hydrazine, and formamide (19). The results here suggest that ethanol does not meet these criteria. In other words, xerogels infiltrated with ethanol are stronger than exposed xerogels because the partial pressure of water inside the xerogels is reduced. Xerogels which are infiltrated with ethanol after exposure to moisture show no reversal in strength because the absorbed ethanol molecules do not displace the already adsorbed water molecules.

Hardness appears to be governed by both the bond strength of the material and its porosity. Unlike strength, hardness is not critically dependent on flaw size distribution. Porous xerogels, with the structure of an infinite covalently bonded network, have hardness values about 350 MPa, as compared to a typical hardness value of 6000 MPa for dense silica glass. There is some reduction of hardness with moisture adsorption which may be at least partly due to the high concentration of surface silanols. Nevertheless, the hardness is less sensitive to moisture than the strength.

Conclusions

Strengths and hardness of silica xerogels have been measured. Strength of about 20 MPa is measured on exposed xerogels which is about the strength measured by others on similar polymerized gels. The xerogels are sensitive to moisture. When water adsorption is prevented by storing samples in ethanol, higher strengths are measured. A hardness of about 350 MPa is measured in all cases. It is safer to say that silica xerogels prepared in this way have mechanical integrity and a level of stability which has been quantified, and that these mechanical properties can now be designed into potential applications.

Table: Strengths and Weibull Parameters
for Silica Xerogels

Material	Population	Sf(MPa)	m	R ²	Hardness (MPa)
-----	-----	-----	---	---	-----
Fresh, exposed xerogel	50	19.3	3.7	.91	350 _{±2}
Outgassed Xerogel	50	32.0	3.7	.96	413 _{±2}
Outgassed, exposed xerogel	50	21.6	2.6	.97	355 _{±3}
Outgassed Xerogel stored in ethanol	20	48.0	3.4	.99	---

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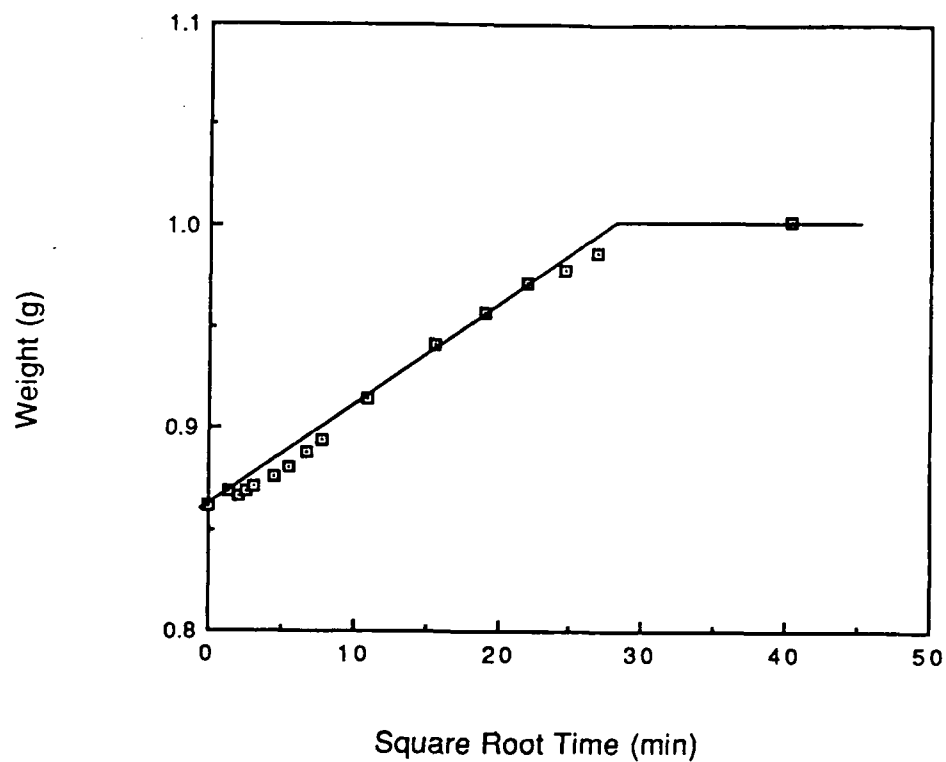


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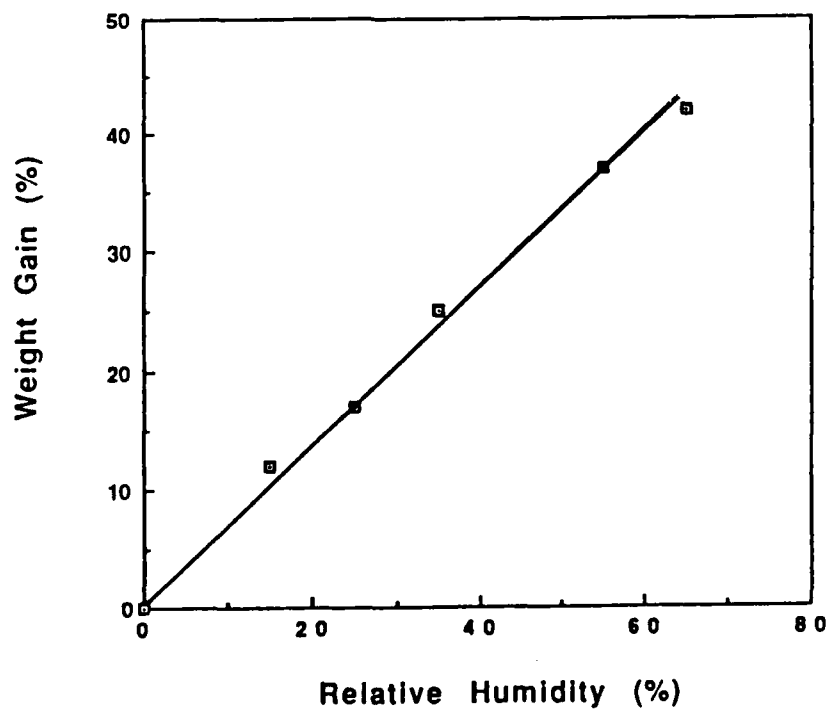


Figure 2: Total weight gain vs relative humidity for silica xerogels exposed for 2 days after outgassing.

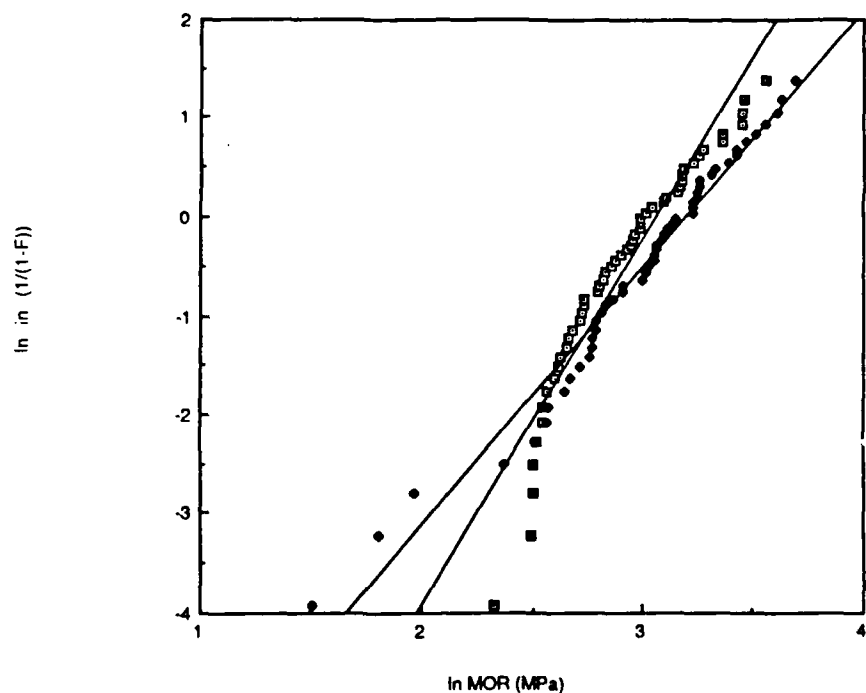


Figure 3: Weibull distribution plot for silica xerogels before outgassing (open box) and after outgassing and exposure (filled diamond).

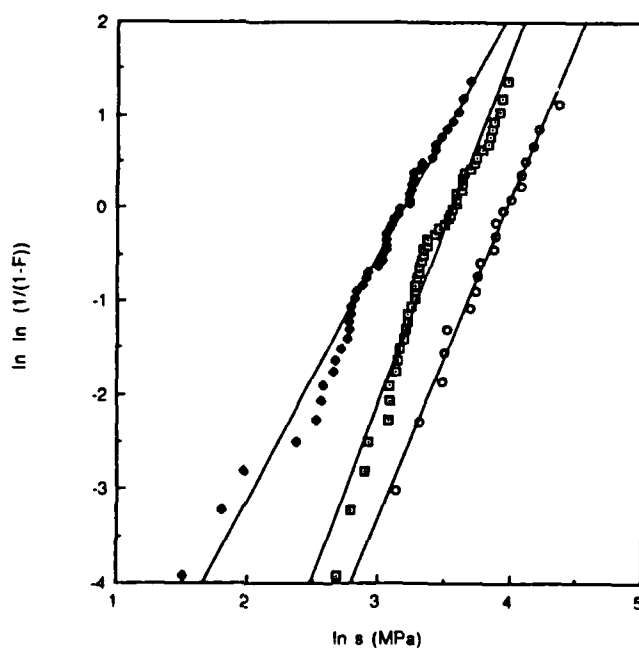


Figure 4: Weibull distribution plot for silica xerogels outgassed and exposed (filled diamond), outgassed and sealed in vials (open box) and stored in ethanol (open circle).